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<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
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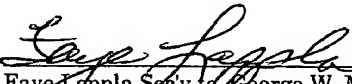
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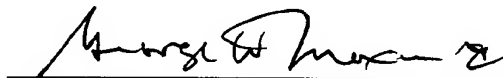
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July 29, 2003

CONTROLLER ELECTRICAL CONDUCTIVITY IN POLYMERS THROUGH THE USE OF CONDUCTIVE AND NON_CONDUCTIVE NANO AND MICROPARTICLES

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ABSTRACT

We have discovered a novel method to control the electrical conductivity of conductive particle filled normally electrically insulating polymers through the use of judicious composition of fillers composed of conductive/non-conductive particles whose sizes may be in the range from micrometer to nanometer. Furthermore, we unexpectedly discovered this technique allows the reduction of percentage of conductive fillers present in the composite while achieving high conductivity levels. Furthermore, we have discovered that products made of such systems exhibit much lower spatial variation in their electrical properties. This is essential in their optimum performance in products with complex shapes.

This discovery provides a novel material preparation procedure wherein the use of conductive particles is greatly reduced while setting and maintaining the electrical conductivity at desired controlled levels.

One of the main applications of electrically conductive polymers is their use as electronic packaging where the dissipation of electrical charges is essential to protect the functionality of the electrical components being contained. However, their presence

causes some unexpected problems. For example it is desirable to have as low a particle generation as possible in order to protect the sensitive components being housed. This is particularly important if the conductive particles contaminate the delicate electronic components. It is therefore desirable to reduce their concentration for this reason as well as for cost reduction purposes. Chemical antistatic sprays or coating are not suitable with a wafer or disk drive assembly environment because of the cleanliness issue. Too high conductivity causes uncontrolled discharge; besides, there is an optimum level of conductivity especially on surface. It has been known recently that the optimal surface conductivity is in the range of 10^{-6} - 10^{-9} S/cm. However, it is very difficult to achieve the optimum conductivity with the conductive particles commonly (they combine the good physical properties of commercial polymers with the relatively high conductivity and low cost) used to transform an insulating polymers into conductive. Besides, to maintain a good performance as conductive material, homogeneous distribution of particle network is counted. Besides, a recent major problem in the packaging industry is particles themselves. The users are trying to refuse using the particles; because, the reason is that they believe the particles expelled from the package becoming free thick and they invade the precision electronic parts and cause a variety of damages.¹⁻¹⁰

In addition to the above-mentioned application, the conductive polymers are increasingly becoming important in such applications as Fuel cells among others. These necessitate high temperature performance in the materials that could be easily accommodated using high temperature polymer matrices with the conductive fillers.

In addition to electrical conductivity, there may be additional advantages for these composites such as improved thermal conductivity.

In a typical application the conductive composite polymers are formed into desired shape through one of the main polymer processing operations such as extrusion, thermoforming, injection molding, and film blowing etc.

MOTIVATION

Most polymers are electrically non-conductors due to their chemical architecture. As a result they are not easily used in applications requiring this property such as electronic packaging, EMI (electromagnetic wave interference) shielding etc.. In order to alleviate this problem several methods have been developed to induce electrical conductivity, these include following: i) Chemical alteration of polymer structure to advantageously induce electrical conductivity (E.g. Poly acetylene) though some of these require doping with other small molecules¹¹⁻¹², ii) More commonly the polymers are compounded with conductive particles that includes, conductive carbon black (CB)¹³⁻²², carbon nano tubes (CNT)²³, metal powders²⁴, flakes⁶, fibers (Nickel, Steel, Al, etc)^{6, 25}, and iii) Polymers are also modified to induce conductivity through ionic conduction mechanism such as PEO-salt complex²⁶⁻²⁸.

Addition of solid particles though induces electrical conductivity may detrimentally affect other performance characteristics of the polymers. Among these are increased melt viscosity during processing, generation of unwanted wear particles that can damage sensitive equipment, increased average density.^{6, 29} It is always desirable to reduce the content of conductive particles to reduce the cost of the final product.

BACKGROUND

The effect of macroscopic inorganic particles such as glass fiber (GF), carbon fiber (CF), carbon black (CB), silica or mica have been studied on the performance of other materials including polymers for nearly a century to attain variety of physical effects. These include enhancement of thermal behavior (e.g. heat distortion temperature), stiffness enhancement, strength enhancement (e.g. Rubber + CB) and thermal and electrical property enhancement. These physical properties are generally strongly dependent on the filler shape, size, rigidity, fill factor and filler distribution in the matrix.¹⁵ It is therefore imperative to use good mixing process to properly disperse these particles in the polymer matrices. The most important issues governing the effect of particles on the physical properties are: particle aggregation and orientation.⁶ This is specifically as a result of processing history either during the mixing or during the shaping operations such as injection molding, thermoforming, etc... Variations in these processes result in variation of properties within each product. The reduction of such variabilities is important for commercial applications.

CB-filled polymeric composites (CB-Com) have been used as industrial filler mainly for coloring, UV absorption, mechanical reinforcement and electrical properties. Of particular note is the enhancement of mechanical properties of rubbers by the inclusion of CB that made the tire manufacturing possible.^{2,9-10}

Another important application for CB is as conductive filler. CB-Com have many advantages such as light weight (compared to metal filler-filled composites), low cost (compare to carbon nano tube or CF-filled composites), good processability over conventional polymers and also useful in many application such as electro-packaging for the high tech industry in function of electrostatic discharge protection (ESD), electro magnetic wave absorption/interference shielding for portable telephone or self temperature controlled heater for various electric parts.^{2,9-10} Although, industry is looking for a new kind of carbonless conductive polymers, none of them have yet been fulfilled the characteristics.

The conditions are such as electrically (semiconductor/ESD range: 10^{-6} - 10^{-9} S/cm), mechanically, cleanliness (including out-gassing controlled by free Styrene Monomer), recycle ability, processability, and cost. Hence, CB content must be as low as possible while the conductivity maintained in ESD range.

Conductivity enhancement by CB in polymers has been an active research area for considerable time. Typically these studies include CB or metal filler in a single matrix to achieve certain conductivities. These are shown in figure (Fig. 1.¹³⁻¹⁴ and Fig. 2.²⁴). As observed in these graphs, the conductivity rapidly begins to increase in a narrow composition range that are identified as Percolation threshold. This is characterized by the fact that conductive particles form a network of conductive paths through the part that allow electrons to follow resulting in conductivity. These curves are typically very steep making conductivity to be very sensitive function of composition. Because of this reason, the control of conductivities at intermediate conductivities is typically difficult. What is desired is to have less steep slope of this conductivity vs. conductive particle concentration curves. This is one of the motivations that lead to the discovery of this patent application.

Along these lines researchers have used variations of polymer compositions to advantageously affect the conductivity. For example the fillers are mixed with immiscible polymer blends.^{3,7,10,21-22,30-32} It was found that dispersibility of the CB depends on each component of the polymer blend, the CB do not disperse in equally in both phases of the polymer blends, instead, they choose stable location in either polymer phase or at their interface (Fig. 3.)^{10,3,7,10,21-22,30-32} A discovery of the CB located in the stable phase or interface, it was found that two-phase immiscible polymer system allowed the reduction of CB content. This phenomenon has been called (double percolation).^{10,30-32} Some of the researchers have also found that polymer blend matrix with adding the CB and GF can be described by a “triple-percolation” which is in three continuities of a GF network, polymer phase encapsulating GF, and CB network.^{1,3,7} This morphology is controlled better by the polymer-filler affinity and CB-polymer interaction factors.^{1,3,7} Besides, researchers have also found that percolation changes substantially at a higher temperature region, melt viscosity of polymer matrices, long processing time, filler size and different pressure/shear rate (dynamic percolation).^{5,9,16,19-20,22}

DESCRIPTION OF INVENTION

In this invention, we have taken the Nylon filled with clay nanocomposites and blended with a series of CB compositions and determined the volumetric conductivity (shown in fig. 4.) as a function of composition. In this figure we also indicate control experiments where nylon 6 matrix is compounded with CB only. The results indicate that we can achieve conductivities at lower concentration of CB and the measurements at multiple locations on compression molded samples indicate that there is significantly better repeatability in conductivity in the molded parts. (see fig. 5.1., 5.2., and 5.3.)

The following shows typical details of the experimental procedures:

Example:

We have prepared a series of Nylon 6+clay obtained from RTP company and blended with a low structure CB in the brabender mixer preheated to 250 degree temperature for 8 minutes Following this process, the molten mixture was removed

from the mixer and with the help of general compression press, compressed in to 0.5×10^3 micrometer thickness sheets.

These sheets were then characterized for their electrical volume conductivities using a Keithley 487 picoammeter equipped with a direct current voltage source at room temperature under ASTM D257 test technique. As shown in the fig. 4., the conductivity starts increasing earlier in the Nylon + clay + CB system.

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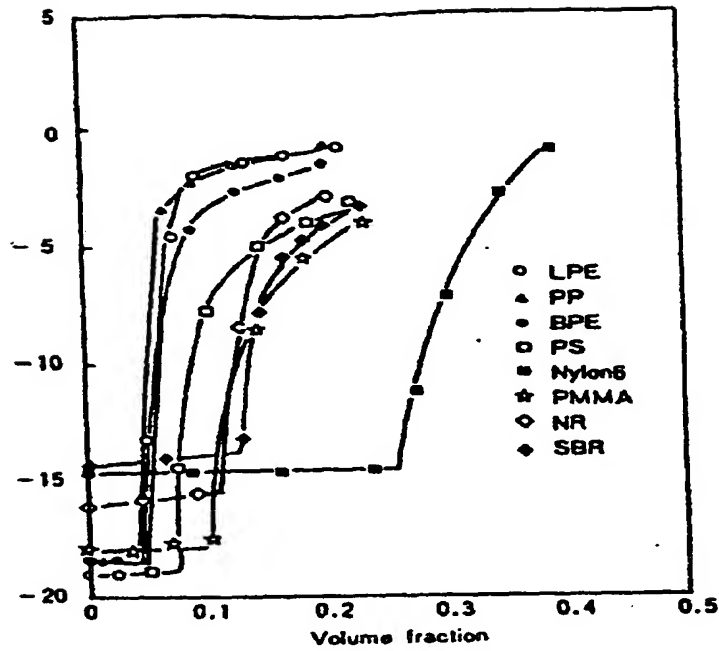


Fig. 1.¹³⁻¹⁴ Electrical conductivity of polymer composites filled with CB particles as a function of CB content. (Conductivity $\log \sigma$ is in S/cm)

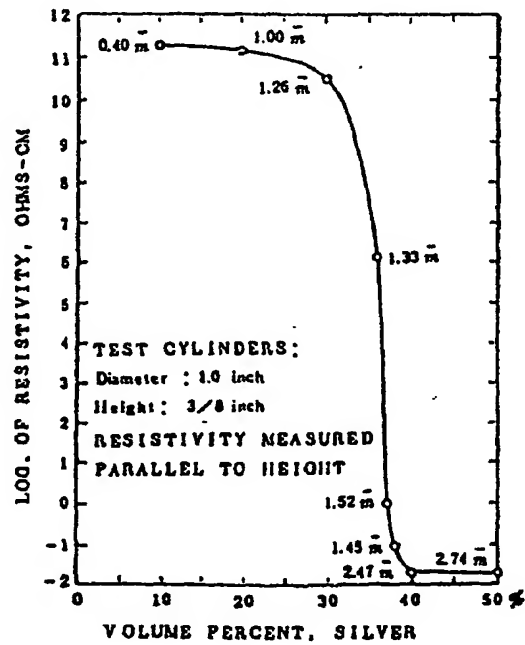


Fig. 2.²⁴ Gurland's result.

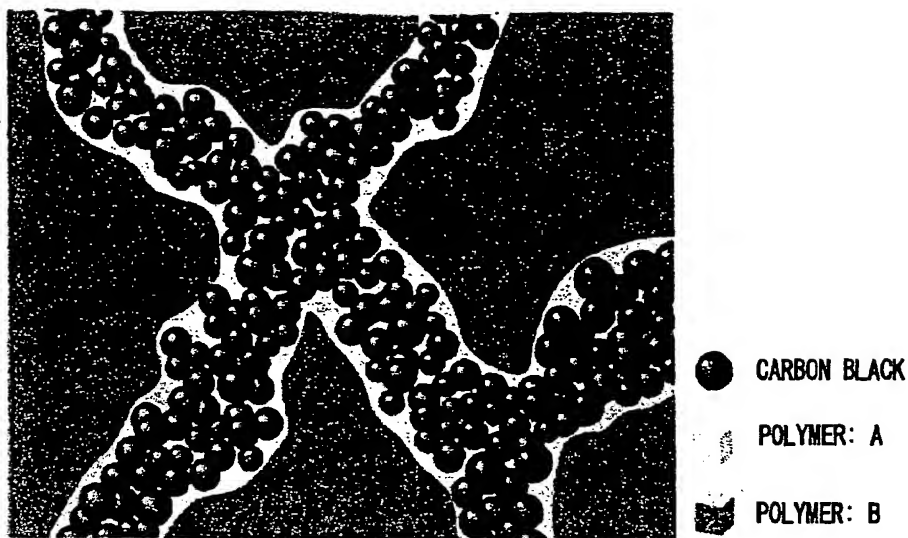


Fig. 3.¹⁰ Schematic representation of double percolation.

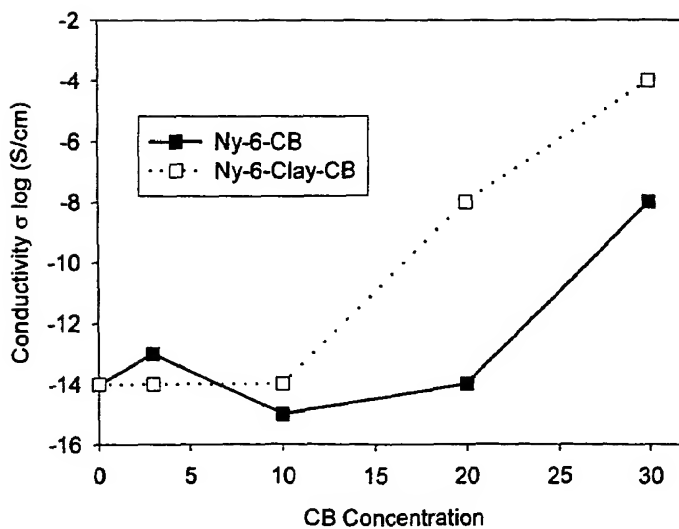


Fig. 4. CB concentration dependency of the room-temperature conductivity for Ny-6/CB and Ny-6-Clay/CB hybrids compression-molded at 250°C for 10min and air-cooled for 5min.

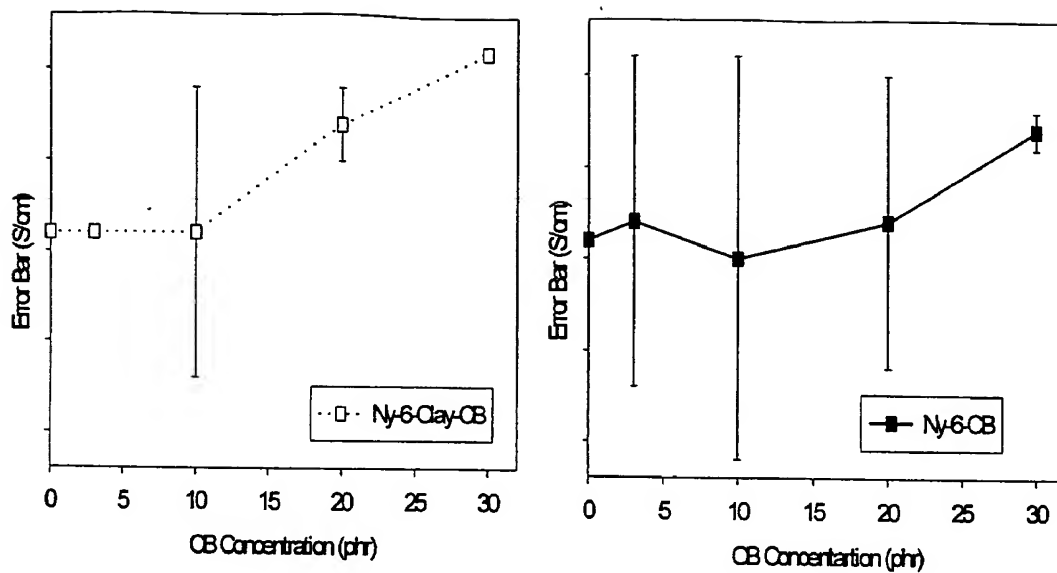


Fig. 5.1. CB concentration dependency of the conductivity error bars for Ny-6/CB and Ny-6-Clay/CB hybrids.

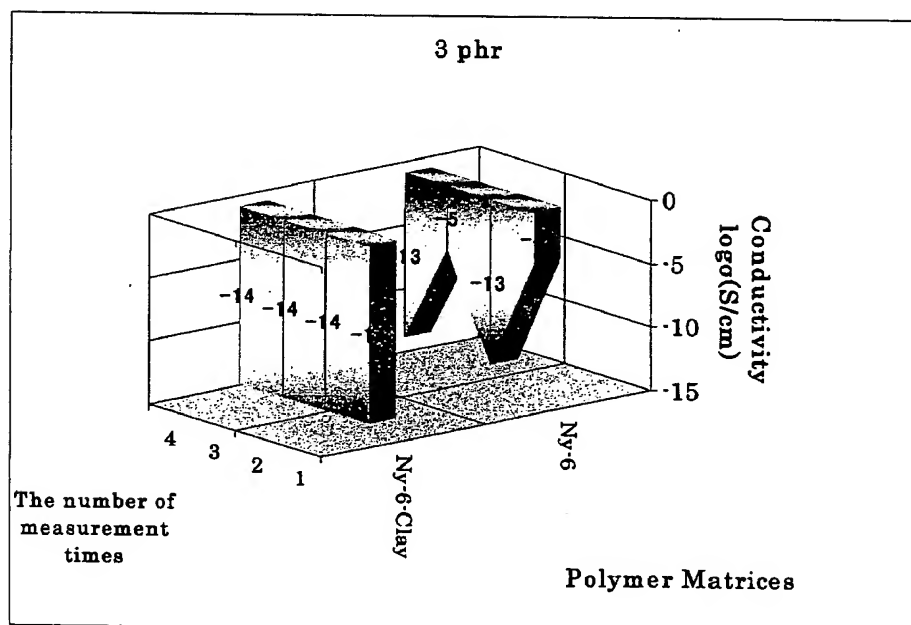


Fig. 5.2. Relation between electrical conductivity and the number of measurement times for Ny-6 and Ny-6-Clay polymer matrices filled with 3 phr CB concentration.

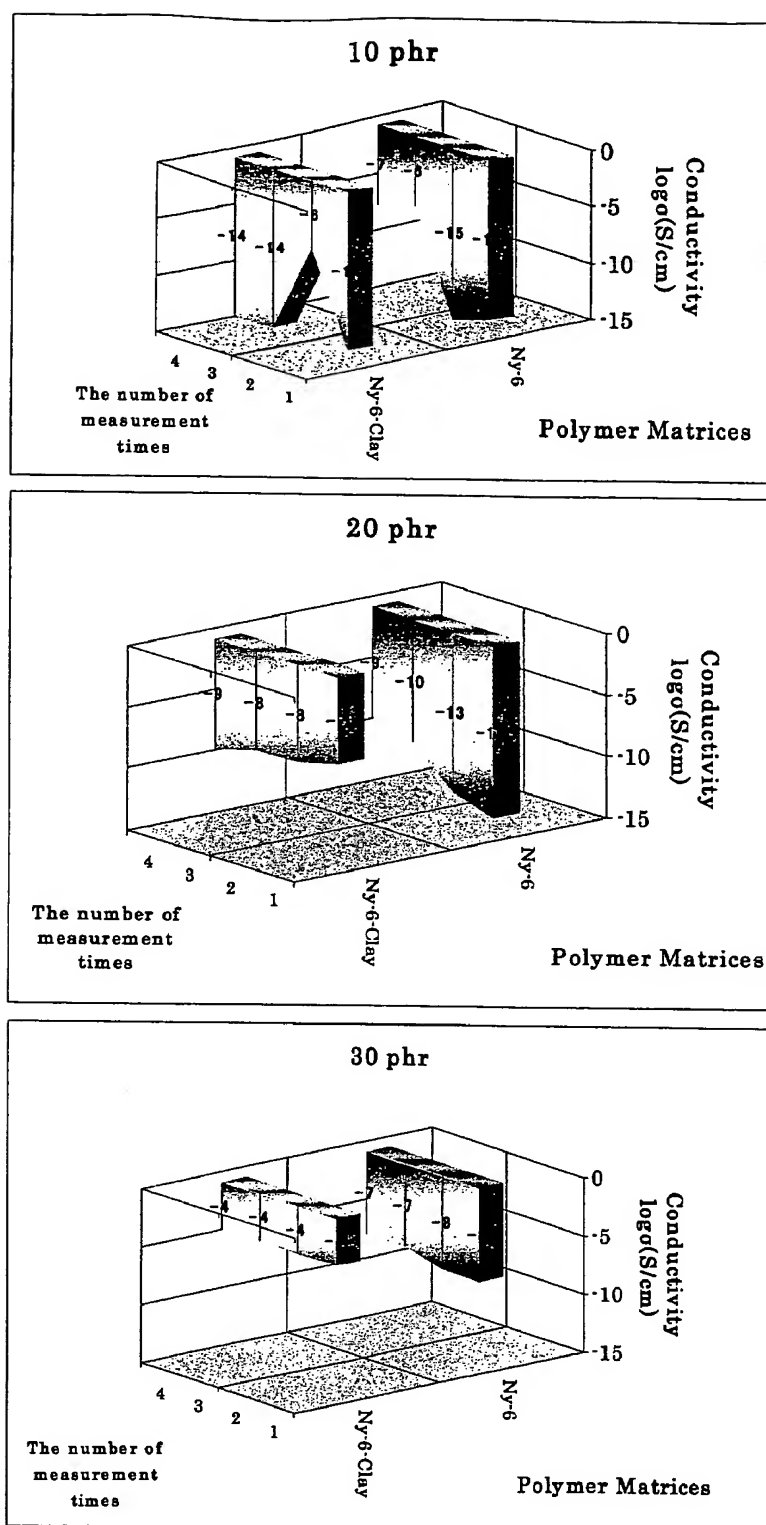


Fig. 5.3 Relation between electrical conductivity and the number of measurement times for Ny-6 and Ny-6-Clay polymer matrices filled with 10 phr, 20 phr, and 30 phr CB concentration respectively.

THE ROLE OF FILLERS AND PROCESSING HISTORY ON ELECTRICAL CONDUCTIVITY OF POLYMERIC NANOCOMPOSITES

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ABSTRACT

Requirements on particle-filled conductive nanocomposites are more involved in filler reduction, reliable electrical properties, and filler dispersion control today. The present study is concerned with advanced percolation phenomenon comprising with the influence of the role of organoclay nanoparticles(nanoclay), and carbon black nanoparticles(CB). We observed that if CB particles are incorporated into a polymer matrix together with nanoclay the percolation threshold shifted to a lower CB content. The advanced percolation phenomenon is due to advantageous thermodynamic interactions between nanoclay/polymer, that accelerated the kinetics of CB network formation.

KEY WORDS: Percolation, Nanocomposites, Electrical conductivity

1. INTRODUCTION

The morphology and properties of filled polymeric composites are greatly influenced by the state of filler dispersion, filler properties (particle size, specific surface area, aggregate structure, and surface chemistry), and polymer-filler interactions. Historically, design of materials with particle filled composites involves a complex balancing act to obtain perfect colloidal balance of filler-filler and the filler-polymer interactions.[1-2]

Electrical property of composite system generally shows sharp break in the relationship between the conductive filler content and the electrical conductivity. This phenomenon called “percolation” and the critical filler content is known as the “percolation threshold(V_f^*)”. For the explanation of this unique phenomenon, numerous investigators developed several concepts from the classical statistical models to chemical thermodynamic models which all well summarized by Lux[2]. The experimental factors under isotropic condition (thermodynamically and rheologically stable) which govern the V_f^* are mostly affected by the geometry/surface conditions of the filler, the melt viscosity/crystallization behavior of the polymer matrix, and the molding time/temperature.[2] These factors are the direct evidence indicating carbon black nanoparticles (CB) in a polymer matrix require time and some sort of energy transformation as their driving force to transfer and form the conductive network.[3] Few investigators report novel percolation phenomenon by reducing CB content in composite systems.[4-7]

Polymer matrix nanocomposites with the exfoliated silicate platelet of organoclay have attracted much attention from both industry and academia due to the unique mechanical and gas barrier properties that are not readily available in conventional composites.[8] Since the silicate platelets of organoclay have polar groups, they have good affinity only with polymers containing polar functional groups. This is one of the reason that nylon-6/organoclay nanocomposites are remarkably compatible, which dramatically improve physical properties due to the small interfacial tension between nylon-6/organoclay, and also the amine end groups of nylon-6 easily formed hydrogen

bonds with the hydroxyl or carboxyl groups grafted onto the large flat surface of the clay platelet.

The present study is concerned with the investigation of the electrical property-CB dispersion relationships in compression-molded CB-filled nylon-6 and filled nylon-6 with organoclay. In this article, we will present our preliminary results obtained from the Voltmeter-Ammeter method using a Galvanometer, Scanning electron microscopy(SEM), and SEM image analysis.

2. EXPERIMENTAL

2.1. Materials and Sample Preparation

Film grade neat nylon-6 and nylon-6/organoclay nanocomposites with 5 vol% organoclay content were purchased RTP Company, USA. CB(Seast G-SVH) was kindly provided by Tokai Carbon Co., LTD., Japan.

Prior to the compounding, each polymers and CB were dried at 80°C for 24 h under vacuum. Compounding was executed in an internal mixer for 10 min at the temperature 245°C under a mixing rate of 60 rpm. Films with thickness of 0.5 mm for the electrical conductivity measurement were compression-molded from the polymer-CB mixtures at 250°C for 10 min under a pressure of 20 MPa, followed by air cooling in room temperature for 5 min.

2.2. Electrical Conductivity Measurements (ASTM D257, and D4496)

The electrical conductivity was measured in the thickness direction of the film using a Keithley 6487 picoammeter equipped with a direct current voltage source. The voltage values were from 0.001 to 500 V. The bulk conductivity of the films was determined by the average conductivity from the four locations of a center region in each film.

2.3. SEM Observations

The state of CB dispersion was observed by means of a field emission type SEM (JEOL). Specimens were freeze-fractured in liquid nitrogen. The freeze-fractured surface was coated by the Polaron high energy silver sputtered device under vacuum atmosphere for 1 min.

2.4. Digital Image Analysis of SEM photographs

Quantitative analysis of the CB dispersion was characterized by the statistical processing of the SEM photographs using the quadrate method and Morishita's distribution index; I_{delta} . [1] The index plays an important role in the characterization of the distribution modes which is given by

$$I\delta = q \cdot \delta \quad (1)[1]$$

with

$$\delta = \frac{\sum_{i=1}^q n_i(n_i - 1)}{N(N - 1)} \quad (2)[1]$$

where q is the number of elemental parts equally divided from the total area of the SEM images; n_i the number of particles in the i th section; and N the total number of particles:

$$N = \sum_{i=1}^q n_i \quad (3)[1]$$

3. RESULTS AND DISCUSSION

Fig.1 shows the electrical conductivity of nylon-6, and nylon-6/organoclay nanocomposites as functions of CB content. The percolation threshold is defined as at a CB content where the first conductive network is formed.[9] However, the formation of conductive network doesn't require direct contact between two CB particles, but only close enough in the order of few nanometers for the electron tunneling. In this article, we define percolation threshold(V_f^*) as 30 phr for filled nylon-6 system, and 20 phr for filled nylon-6/organoclay(5vol%) system, respectively as indicated by the arrows. The unit, phr, means CB weight per 100 parts of resin.

Generally, the V_f^* of nylon-6 is much higher than other polymers such as polyolefins.[10] This is due to the polarity of nylon-6(large surface tension), that decreases the interfacial tension between CB and polymer. What is of striking in Fig.1 is that despite the same film grade nylon-6 and CB were used for both composites in this study, the V_f^* dramatically shifted to a lower CB content (20 phr) by the presence of organoclay. Besides, the electrical conductivity and its data in CB-filled nylon-6/organoclay system are higher and reliable than the filled nylon-6 system. This may suggest that although CB particles have large restriction of their mobility, the existence of strong hydrogen bonding between the hydroxyl groups in large surface organo-platelet and polar groups in nylon-6 under high temperature which is strong enough to attract the CB toward the platelet that accelerates the kinetics of CB network formation through Brownian motion. Incorporation of CB into the polar polymer systems causes less colloidal unbalance due to their availability of compatibilization; thus, CB-CB interaction force is very weak [3]; moreover, we chose low structure CB that generally they have a difficulty to disperse and develop percolating network by self-agglomeration(Fig.3).

Dispersion can be defined as the distribution of filler aggregates and inter-particle(or inter-aggregate) distance in the polymer matrices.[1] Fig.2 shows SEM images of 20 phr CB content in each (a) nylon-6, and (b) nylon-6/organoclay(5vol%) systems from four compression molded parts at low magnifications, respectively where the gray/white areas represent the nylon-6 matrix and the black dots are CB. It is clearly observed that CB in Fig.2(b) forms a well-developed fish-net morphology and co-continuous CB network structure. Whereas in the nylon-6 system forms relatively scattered CB aggregates morphology. Fig.3 [11] gives the TEM images of (a) the typical high structure CB and (b) the CB which we used in this study. It is clearly observed from Fig.3(a) that high structure CB have small particle size/high surface area, indicating many primary particles with "branching" and "chaining" morphology, whereas CB in Fig.3(b) have large particle size/low surface area with low structure, indicating more independent aggregates constructed by fewer primary particles. This comparison indicates that the distance of gaps between the primary aggregates in Fig.3(b) is larger than Fig.3(a) which brings greater difficulty of electrons hopping those gaps through the tunneling-conduction mechanism. This may explain how difficult for the low structure CB to form continuous conductive network especially in polar polymers.

Quantitative analysis of the state of CB dispersion is characterized by the statistical processing of image analysis using high magnification SEM images with the quadrate method and Morishita's distribution index[1]. The index is one of the most useful statistical method in which the total area of the SEM pattern is divided into small elementary parts with an equal area and the number of the points in each element is calculated. More details are explained in Fig.4[1]. Fig.5 shows the relationships between

Morishita's index and the dividing number q obtained from the SEM images of 10, and 20 phr CB-filled nylon-6, and filled nylon-6/organoclay(5vol%) systems. For the both CB contents of filled nylon-6 systems show almost $I_{delta} = 1$ indicating *Poisson's* distribution, which showing schematically in Fig.4(a) and it is also correlated to the SEM images. However by the presence of organoclay, 10 phr CB content shows an increase of $I_{delta} > 1$, which corresponds to Fig.4(d), whereas at 20 phr CB content shows a large $I_{delta} > 1$ with a sharp maximum peak, which corresponds to Fig.4(f). This observation indicates that for 10 phr CB content it is aggregated distribution in small size aggregates and CB are dispersed in *Poisson's* mode; however, at 20 phr CB content it is also aggregated distribution in small size aggregates but the CB particles are dispersed in regular mode. As a result, the state of CB dispersion in 20 phr CB-filled nylon-6/organoclay(5vol%) system shows not only network formation but also uniform which explained the reasons of higher and reliable electrical conductivity in Fig.1.

Fig.6 shows the histogram of the distribution of average nearest neighbour length for 20 phr CB content filled nylon-6, and filled nylon-6/organoclay(5vol%) systems. It is clear that filled nylon-6 system has a broad nearest neighbour length distribution, whereas it is more narrow distribution with the presence of organoclay. What is of most interest in Fig.6 is that the peak(400 nm) of the histogram in the filled nylon-6 system which indicated by the arrow shifted to a shorter nearest neighbour length(200 nm) by the presence of organoclay. The average travel distance for CB which affected by the interactions between organoclay and nylon-6 matrix is 200 nm.

4. CONCLUSIONS

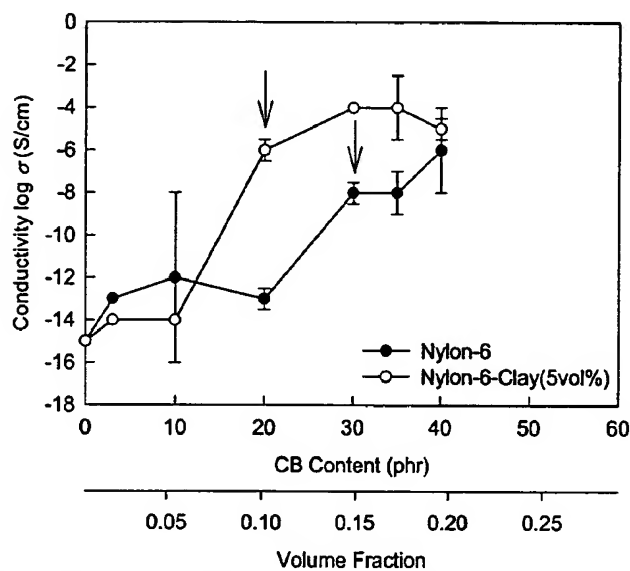
The compression-molded CB-filled nylon-6 system shows percolation phenomenon. The percolation threshold shifts to a lower CB content by the presence of organoclay. The electrical conductivity in nylon-6/organoclay system is higher and reliable than the nylon-6 system. Here, we propose that the interactions between organoclay/nylon-6 under high temperature bring strong hydrogen bonding between the hydroxyl groups in large surface of organoclay and polar groups in nylon-6 which is strong enough to attract CB during a process of network formation through Brownian motion. Despite we used low structure CB, the existence of the strong chemical thermodynamic interaction allows CB to travel 200 nm in average distance toward the organo-platelet that accelerates the kinetics of percolation and forms well network arrangements along the platelet geometry under stable colloidal balance. This novel phenomenon as "advanced percolation" does not fit into any known categories of percolation behavior in the published literature[12].

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Fig.1 CB content dependency of the room-temperature conductivity for CB-filled nylon-6, and filled nylon-6/organoclay systems.

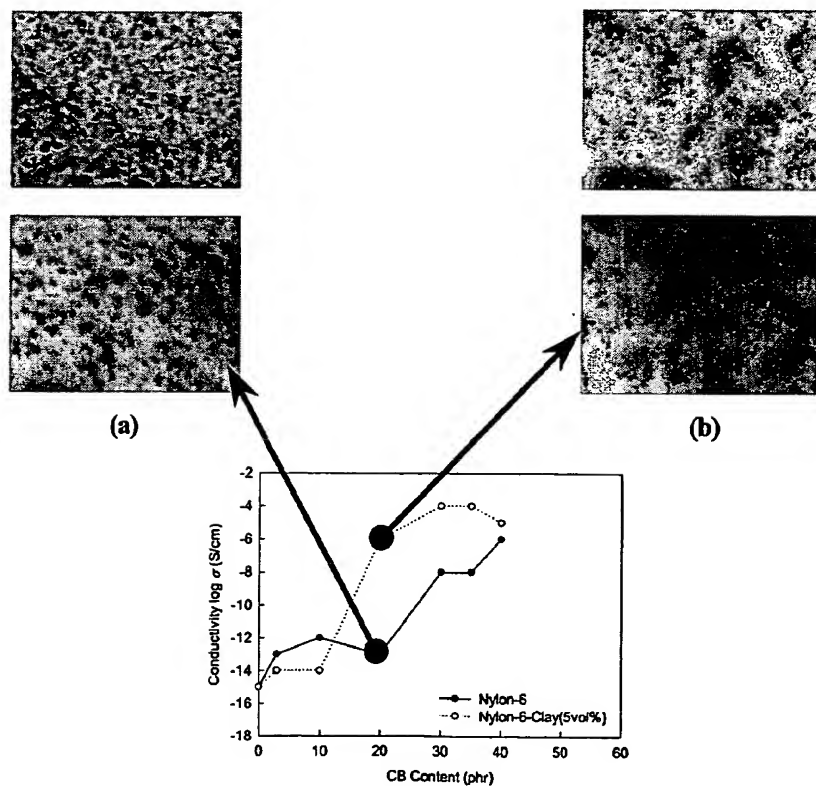


Fig. 2 SEM images for CB(20phr)-filled (a) nylon-6 and (b) nylon-6/organoclay(5vol%) systems at low magnifications (x 7,500-10,000).

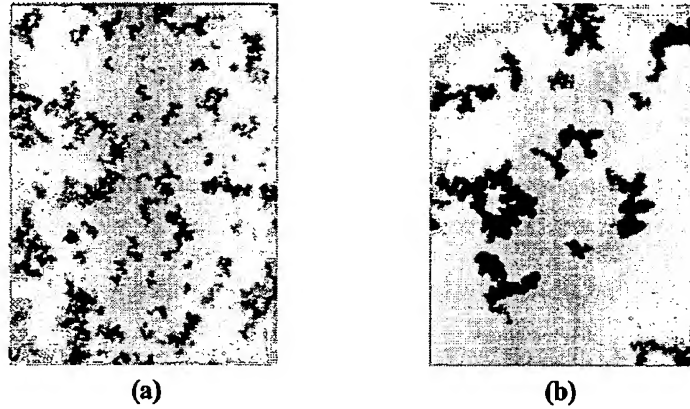


Fig. 3[11] TEM observation (x 60,000) of (a) typical fine particle size/high structure CB and (b) low structure CB used in this study.(Used with the permission of the Tokai-Carbon Co., LTD.)

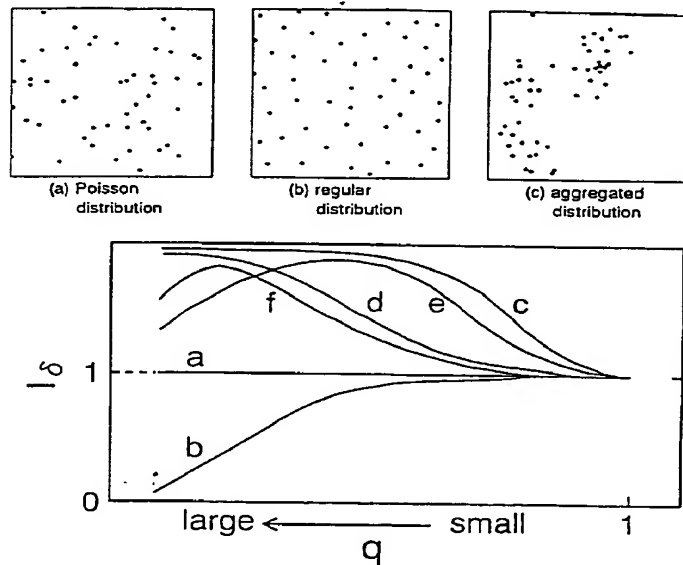


Fig.4[1] Schematical representation of the relationship between Morishita's I_{deta} value and dividing number q for various distribution modes of primary aggregates. It shows the model of 50 particles dispersing in equal area and it is corresponding to the typical distribution modes of each particle. When it is $I_{deta} = 1$, it shows *Poisson's* distribution as linear in (a). When it is $I_{deta} < 1$, the curve shows regular

distribution as curve in (b) which the dispersion state is always homogeneous and I_{delta} gradually decreases with an increasing q value. Finally when it is $I_{delta} > 1$, it shows aggregated distribution as curve in (c-f) which I_{delta} increases as the q value increases: (c) aggregated distribution in which the size of each aggregate is large and the primary particles are dispersed in *Poisson's* mode, (d) aggregated distribution in which the size of each aggregate is small and the primary particles are dispersed in *Poisson's* mode, (e) aggregated distribution in which the size of each aggregate is large and the primary particles are dispersed in regular mode, and (f) aggregated distribution in which the size of each aggregate is small and the primary particles are dispersed in regular mode.

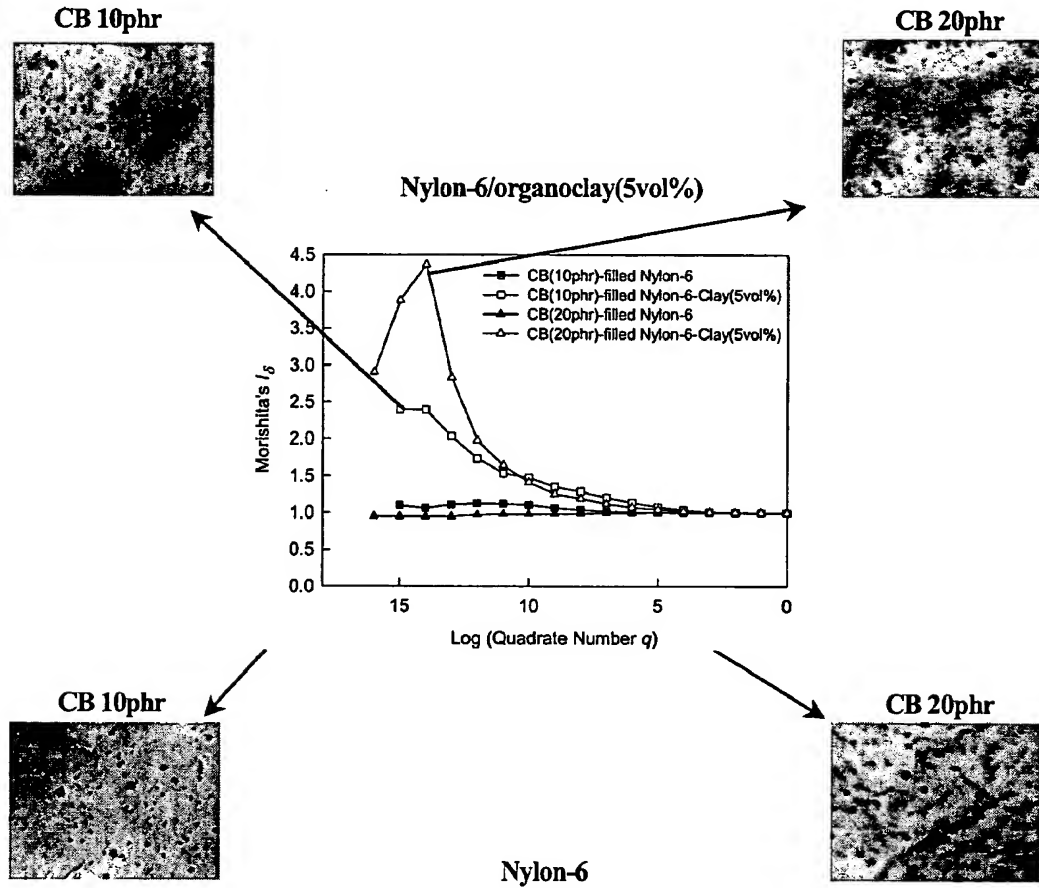


Fig.5 Relationship between Morishita's I_{delta} value and dividing number q for 10 and 20 phr CB-filled nylon-6, and nylon-6/organoclay(5vol%) systems at high magnification (x 15,000) of SEM images.

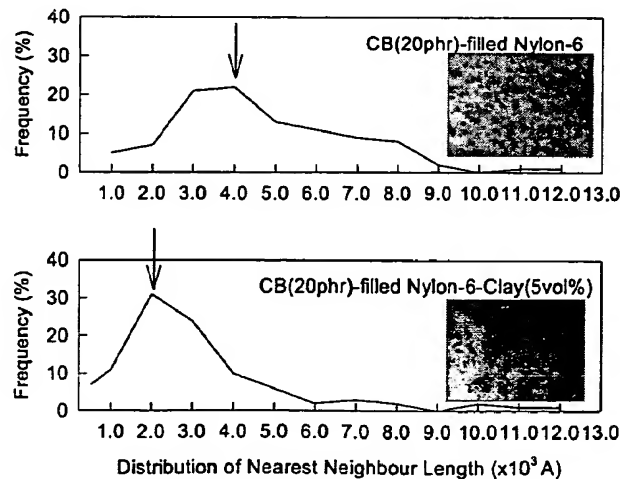


Fig.6 Histogram of the distribution of nearest neighbour length for 20 phr CB-filled nylon-6, and filled nylon-6/organoclay(5vol%) systems.

BIOGRAPHY

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His current interests are processing- structure and property relationships and their computer simulation, particularly the effect of stress history on the development of structure in various polymer processes such as melt spinning, blow molding, welding, multiaxial stretching. In addition, he is currently active in developing strategies for hierarchical structural control of continuous processes such as film casting and fiber spinning. In his past he has developed a series of highly instrumented processing instruments including spin and vibration welding machines, Real time spectral birefringence monitoring system for heat setting, Real time birefringence-true stress-true strain measurement system during uniaxial as well as biaxial stretching deformation of polymeric films.

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He received BS degree in Industrial Technology from Nihon University, where he engaged in research on CB-filled conductive composites for electro-packaging application under Dr. H. Hojo. During this time, he did experiment at Dr. M. Sumita research laboratory of Tokyo Institute of Technology, which gave him inspiration to go on for the graduate school at the University of Akron, where currently he engages in research on conductive nanocomposites for polymer processing at Dr. M. Cakmak research group.

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